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Synthesis and structure of sodium 1-alkoxy-1,4-dioxo-2-alkenolates and *bis*-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) based on them

© Elena A. Kunavina*, Sergey A. Peshkov*, Aybek Yu. Iskandarov**

*Orenburg State University, Orenburg, Russian Federation
**Tashkent State Pedagogical University, Tashkent, Uzbekistan

Abstract: *A priority task in contemporary organic chemistry consists in the synthesis of practically useful metal complexes having carbonyl-containing ligands. The present article details the isolation of several new bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) via complex formation of metal salts of (zinc (II), copper (II) and nickel (II)) with sodium 1-alkoxy-1,4-dioxo-2-alkenolates obtained by condensation of alkyl (aryl) methyl ketones with dialkyl oxalates in the presence of sodium or sodium hydride as a condensing reagent. The structure of the synthesised sodium oxoenolates and metal complexes was confirmed by spectral analysis methods (IR, NMR ^{1}H-, NMR ^{13}C-spectroscopy and mass spectrometry). In the IR spectra of the solid samples of the isolated compounds, stretching vibrations bands of ester carbonyl groups were identified, as well as high-intensity ether bands due to the vibrations of C-O-C bonds. For compounds containing aromatic fragments, bands corresponding to vibrations of monosubstituted benzene rings were found in the IR spectra. The NMR spectra of ^{1}H of sodium oxoenolates and metal complexes recorded in DMSO-d_6 demonstrated characteristic signals of ethoxy and n-butoxy fragments, methine protons, as well as protons of aromatic rings. Chemical shifts of carbon atoms in the NMR spectra ^{13}C of sodium oxoenolates correspond well to the reference values. In the mass spectra of synthesised compounds recorded in electrospray mode, signals of protonated and cationised molecules were observed $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$, $[M+K]^+$. Using quantum chemical methods, the models of the obtained compounds were constructed along with a calculation of the formation energies and dissociation constants. Optimisation of the geometric parameters of the equilibrium states of sodium oxoenolate and metal complexes was carried out using the following two methods: density functional theory (DFT) and self-consistent field (SCF). The relative formation energies indicate high stability of the synthesised substances, while, according to the data obtained, copper complexes are characterised by greater stability in the gas phase as compared to zinc and nickel.*

Keywords: *sodium oxoenolates, metal complexes, synthesis, spectral analysis*

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Синтез и строение 1-алкокси-1,4-диоксо-2-алкенолятов натрия и *бис*-(4-алкил(арил)-1-оксо-1-алкоксиалкан-2,4-дионато)металлов(II) на их основе

Е.А. Кунавина*, С.А. Пешков*, А.Ю. Искандаров**

*Оренбургский государственный университет,
г. Оренбург, Российская Федерация
**Ташкентский государственный педагогический университет,
г. Ташкент, Узбекистан

Резюме: *Синтез практически значимых металлокомплексов с карбонилсодержащими лигандами является приоритетной задачей современной органической химии. Комплексообразованием 1-алкокси-1,4-диоксо-2-алкенолятов натрия, полученных конденсацией алкил(арил)метилкетонов с диалкилоксалатами в присутствии в качестве конденсирующего реагента натрия или гидрида натрия, с солями металлов (цинка(II), меди(II) и никеля(II)) выделены новые бис-(4-алкил(арил)-1-оксо-1-алкоксиалкан-2,4-дионато)металлы(II). Строение синтезированных оксоенолятов натрия и металлокомплексов подтверждено спектральными методами анализа (ИК-, ЯМР* ^{1}*Н-, ЯМР* ^{13}*С-спектроскопии и масс-спектрометрии). В ИК-спектрах твердых образцов выделенных соединений обнаружены полосы валентных колебаний сложноэфирных карбонильных групп, а также эфирные полосы высокой интенсивности, обусловленные колебаниями связей С-О-С. Для соединений, содержащих ароматические фрагменты в ИК-спектрах, найдены полосы, отвечающие колебаниям монозамещенных бензольных колец. В спектрах ЯМР* ^{1}*Н оксоенолятов натрия и металло-комплексов, записанных в ДМСО-*d_6*, присутствуют классические сигналы этокси- и н-бутоксифрагментов, метиновых протонов, а также протонов ароматических колец. Химические сдвиги углеродных атомов в спектрах ЯМР* ^{13}*С окоенолятов натрия хорошо сопоставимы со справочными значениями. В масс-спектрах синтезированных соединений, зарегистрированных в режиме электрораспыления, наблюдаются сигналы протонированных и катионированных молекул* $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$, $[M+K]^+$. *С использованием квантово-химических методов построены модели полученных соединений и рассчитаны энергии образования и константы диссоциации. Оптимизация геометрических параметров равновесных состояний оксоенолятов натрия и металлокомплексов произведена в рамках двух методов: теории функционала плотности (DFT) и самосогласованного поля (SCF). Относительные величины энергий образования свидетельствуют о высокой стабильности синтезированных веществ, при этом, согласно полученным данным, большей устойчивостью в газовой фазе характеризуются медные комплексы.*

Ключевые слова: *оксоеноляты натрия, металлокомплексы, синтез, спектральный анализ*

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INTRODUCTION

The chemistry of metal complexes is an extensive and rapidly developing field due to the multifunctionality and practical significance of these materials. Among the interesting properties of metal-complex compounds are included biological, pharmacological, photochemical and photophysical attributes [1–15]. Additional some metal complexes have been successfully used in the development of novel nanoscale structures [16]. Among metal complexes having organic ligands, the least studied are those based on polycarbonyl systems with conjugated α- and β-dioxo links. In order to expand the number of available metal complexes having carbonyl-containing ligands, the present study set out to synthesise new representative compounds and evaluate their stability using quantum chemical methods.

EXPERIMENTAL

*Synthesis of 4-alkyl(aryl)-1-alkoxy-1,4-dioxo-2-sodium alkenolates (**1**). General procedure.* 0.58 g (25 mmol) of sodium was gradually added with stirring to a mixture of 25 mmol of the corresponding methyl ketones (3-methylbutanone-2 or acetophenone), 25 mmol of dialkyl oxalates (di-*n*-butyloxalate or diethyl oxalate) and 50–100 ml of benzene or toluene. The reagent mixture was boiled for 1.5–2 h (TLC control) in a round bottom flask with reflux condenser. Following evaporation of solvent, the obtained oxoenolates were washed with ether.

*1-Butoxy-5-methyl-1,4-dioxo-2-hexene-2-sodium-olate (**1a**).* Yield 84 %, melting point (t_{melt}) – 118–122 °C. IR spectrum, ν, cm^{-1}: 2959 ν_{as} (CH_3), 2931 ν_{as} (CH_2), 1698 (C^1=O), 1625 (C^4=O, C=C), 1379 δ (CH_3), 1267 ν (C-O-C) 951, 770 δ (CH). NMR spectrum ^{1}H, δ, ppm (DMSO-d_6): 0,91 t (3H, $O(CH_2)_3CH_3$, J_{HH} 7,7 Hz), 0,98 d (6H, $(CH_3)_2CH$), 1,35 m (2H, $OCH_2CH_2CH_2CH_3$), 1,60 m (2H, $OCH_2CH_2CH_2CH_3$), 2,40 m (1H, $(CH_3)_2CH$), 4,05 t (4H, $2OCH_2CH_2CH_2CH_3$, J_{HH} 7,2 Hz), 5,65 s (1H, CH). NMR spectrum ^{13}C, δ_C, ppm (DMSO-d_6): 13,5 ($OCH_2CH_2CH_2CH_3$), 18,6 ($OCH_2CH_2CH_2CH_3$), 19,8 ($(CH_3)_2CH$), 20,0 ($OCH_2CH_2CH_2CH_3$), 30,1 ($(CH_3)_2CH$), 63,7 ($OCH_2CH_2CH_2CH_3$), 93,6 (CH), 167,0 (CONa), 168,7 ($COOC_4H_9$), 199,4 ($(CH_3)_2CHCO$). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$,%): 237.1099 (62) $[M+H]^+$, 259.0914 (47) $[M+Na]^+$. Calculated: for $C_{11}H_{18}O_4Na$ – 237.1097; for $C_{11}H_{17}O_4Na_2$ – 259.0917.

*Sodium 1,4-dioxo-4-phenyl-1-ethoxy-2-buten-2-olate (**1b**).* Yield – 85 %, t_{melt} – 156–160 °C. IR spectrum, ν, cm^{-1}: 3060 ν (C-H, Ar), 2979 ν_{as}

(CH_3), 2929 ν_{as} (CH_2), 2871 ν_s (CH_2), 1687 ν (C^1=O), 1623 ν (C^4=O), 1575 ν (C=C), 1505 ν (C=C, Ar), 1390, 1364 δ (CH_3), 1231 ν (C-O-C), 1097 δ (CH, Ar), 950-753 (CH). NMR spectrum ^1H, δ, ppm (DMSO-d_6): 1.26 t (3H, $COOCH_2CH_3$, J_{HH} 7.4 Hz), 4.17 q (2H, $COOCH_2CH_3$, J_{HH} 7.4 Hz), 6.42 s (1H, CH), 7.29–7.51 m (3H, $C^{3'}H$, $C^{4'}H$, $C^{5'}H$ in C_6H_5), 7.82 d (2H, $C^{2'}H$, $C^{6'}H$ in C_6H_5). NMR spectrum ^{13}C, δ_C, ppm (DMSO-d_6): 14,0 (OCH_2CH_3), 60,3 (OCH_2CH_3), 92,0 (CH), 126,4 ($C^{2'}$ and $C^{6'}$ in C_6H_5), 128,1 ($C^{3'}$ and $C^{5'}$ in C_6H_5), 129,8 ($C^{4'}$ in C_6H_5), 142,2 ($C^{1'}$ in C_6H_5), 167,2 (CONa), 170,6 ($COOC_2H_5$), 185,4 (C_6H_5CO). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$, %): 243.0624 (38) $[M+H]^+$, 265.0443 (82) $[M+Na]^+$. Calculated: for $C_{12}H_{12}O_4Na$ – 243.0628; for $C_{12}H_{11}O_4Na_2$ – 265.0447.

*Synthesis of bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato)-metals (II) (**2a–2e**). General procedure.* A solution of 1.0 mmol (0.18 g) zinc acetate, 1.0 mmol (0.18 g) of copper acetate or 1.0 mmol (0.24 g) of nickel chloride hexahydrate in 30–50 ml of water was added with stirring to a solution of 2.0 mmol of sodium 4-alkyl(aryl)-1-alkoxy-1,4-dioxo-2-alkenolates (**1a** or **1b**) in 30–50 ml of water for preparation of compounds **2a** and **2d**, **2b** and **2e**, **2c** and **2f**, correspondingly. After 30 minutes, the as-formed precipitate was filtered off and recrystallised from ethanol. The yields were not optimised.

*Bis-(1-butoxy-5-methyl-1-oxohexane-2,4-dionato) zinc (II) (**2a**).* Yield – 47 %, t_{melt} – 102–104 °C. IR spectrum, ν, см$^{-1}$: 2959 ν_{as} (CH_3), 2933 ν_{as} (CH_2), 1725 ν ($COOC_2H_5$), 1599 ν (C=C), 1455 δ_{as} (CH_3), 1267 ν (C-O-C), 822, 781 δ (CH). NMR spectrum ^1H, δ, ppm (DMSO-d_6): 0,91 t (6H, $2COOCH_2CH_3$, J_{HH} 7,6 Hz), 0,98 d (12H, $2(CH_3)_2CH$, J_{HH} 7,7 Hz), 1,35 m (4H, $2OCH_2CH_2CH_2CH_3$), 1,59 m (4H, $2OCH_2CH_2CH_2CH_3$), 2,40 m (1H, $(CH_3)_2CH$), 4,06 t (2H, $OCH_2CH_2CH_2CH_3$, J_{HH} 7,2 Hz), 5,64 s (2H, 2CH). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$, %): 491.1616 (34) $[M+H]^+$, 508.1887 (38) $[M+NH_4]^+$, 513.1436 (64) $[M+Na]^+$. Calculated: for $C_{22}H_{35}O_8Zn^+$ – 491.1618; for $C_{22}H_{38}O_8NZn^+$ – 508.1883; for $C_{22}H_{34}O_8NaZn^+$ – 513.1437.

*Bis-(1-butoxy-5-methyl-1-oxohexane-2,4-dionato) copper (II) (**2b**).* Yield – 38 %, t_{melt} – 190–192 °C. IR spectrum, ν, cm^{-1}: 2961 ν_{as} (CH_3), 2934 ν_{as} (CH_2), 1722 ν ($COOC_2H_5$), 1582 ν (C=C), 1456 δ_{as} (CH_3), 1317 ν (C-O-C), 823, 796 δ (CH). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$, %): 512.1443 (46) $[M+Na]^+$, 528.1182 (34) $[M+K]^+$. Calculated: for $C_{22}H_{34}O_8NaCu^+$ – 512.1442; for $C_{22}H_{34}O_8KCu^+$ – 528.1181.

*Bis-(1-butoxy-5-methyl-1-oxohexane-2,4-dionato) nickel (II) (**2c**).* Yield – 34 %, t_{melt} – 98–100 °C. IR spectrum, ν, cm^{-1}: 2958 ν_{as} (CH_3), 2933 ν_{as} (CH_2), 1724 ν ($COOC_2H_5$), 1598 ν (C=C), 1454 δ_{as} (CH_3), 1269 ν (C-O-C), 843, 777 δ (CH). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$, %): 485.1682 (65) $[M+H]^+$, 507.1498 (32) $[M+Na]^+$. Calculated: for $C_{22}H_{35}O_8Ni^+$ – 485.1680; for $C_{22}H_{34}O_8NaNi^+$ – 507.1499.

*Bis-(1-oxo-4-phenyl-1-ethoxybutane-2,4-dionato) zinc (II) (**2d**).* Yield 43%, t_{melt} – 130–131 ºC. IR spectrum, ν, cm^{-1}: 2971 ν_{as} (CH_3), 1726 ν ($COOS_2H_5$), 1597, 1575 ν (C=C), 1519, 1464 ν (C=C, Ar), 1429 δ_{as} (CH_3), 1274 ν (C-O-C), 1170 δ_{planar} (CH, Ar), 770, 752 $\delta_{non-planar}$ (CH, Ar). NMR spectrum ^1H, δ, ppm (DMSO-d_6): 1,27 t (6H, $2COOCH_2CH_3$, J_{HH} 7,4 Hz), 4,18 q (4H, $2COOCH_2CH_3$, J_{HH} 7,4 Hz), 6,42 s (2H, 2CH), 7,24-7,52 m (6H, $C^{3'}H$, $C^{4'}H$, $C^{5'}H$ in $2C_6H_5$), 7,82 d (4H, $C^{2'}H$, $C^{6'}H$ in $2C_6H_5$). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$,%): 503.0678 (80) $[M+H]^+$, 520.0945 (53) $[M+NH_4]^+$, 525.0497 (100) $[M+Na]^+$, 541.0235 (22) $[M+K]^+$. Calculated: for $C_{24}H_{23}O_8Zn^+$ – 503.0679; for $C_{24}H_{26}O_8NZn^+$ – 520.0944; for $C_{24}H_{22}O_8NaZn^+$ – 525.0498; for $C_{24}H_{22}O_8KZn^+$ – 541.0238.

*Bis-(1-oxo-4-phenyl-1-ethoxybutane-2,4-dionato) copper (II) (**2e**).* Yield – 42 %, t_{melt} – 125–127 °C. IR spectrum, ν, cm^{-1}: 2976 ν_{as} (CH_3), 1728 ν ($COOC_2H_5$), 1592 ν (C=C), 1564, 1514, 1456 ν (C=C, Ar), 1434 δ_{as} (CH_3), 1272 ν (C-O-C), 1142 δ_{planar} (CH, Ar), 769, 743 $\delta_{non-planar}$ (CH, Ar). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$,%): 502.0685 (22) $[M+H]^+$, 519.0948 (98) $[M+NH_4]^+$, 524.0503 (100) $[M+Na]^+$, 540.0243 (48) $[M+K]^+$. Calculated: for $C_{24}H_{23}O_8Cu^+$ – 502.0683; for $C_{24}H_{26}O_8NCu^+$ – 519.0949; for $C_{24}H_{22}O_8NaCu^+$ – 524.0503; for $C_{24}H_{22}O_8KCu^+$ – 540.0242.

*Bis-(1-oxo-4-phenyl-1-ethoxybutane-2,4-dionato) nickel (II) (**2f**).* Yield – 38 %, t_{melt} – 140–143 °C. IR spectrum, ν, cm^{-1}: 2954 ν_{as} (CH_3), 1729 ν ($COOC_2H_5$), 1595, 1572 ν (C=C), 1519, 1456 ν (C=C, Ar), 1422 δ_{as} (CH_3), 1269 ν (C-O-C), 1146 δ_{planar} (CH, Ar), 771, 745 $\delta_{non-planar}$ (CH, Ar). Mass spectrum (ESI-TOF), *m/z* (*I* $_{rel}$,%): 497.0745 (56) $[M+H]^+$, 519.0561 (42) $[M+Na]^+$. Calculated: for $C_{24}H_{23}O_8Ni^+$ – 497.0741; for $C_{24}H_{22}O_8NaNi^+$ – 519.0560.

IR spectra of compounds **1a, 1b** were recorded on a Bruker Alpha FTIR spectrometer; ATR mode, ZnSe crystal IR spectra of compounds **2a–2e** were recorded on a Vertex 70 IR Fourier spectrometer (Bruker, Germany): range – 400–4000 cm^{-1}, resolution – 2 cm^{-1}, number of scans of the background and sample – 32, ATR mode, diamond crystal. NMR spectra ^1H of the compounds **1a, 1b, 2a** and **2d** and NMR ^{13}C of the compounds **1a** and **1b** in DMSO-d_6 were obtained using NMR Fourier spectrometer Bruker AVANCE II (400 MHz), internal standard – TMS. Mass spectra of the compounds **1**, **2** were recorded on a quadrupole-time-of-flight ultra-high-resolution mass spectrometer Orbitrap Elite, MicroTof Bruker Daltonics. Positive ions were detected in the electrospray ionisation (ESI) mode. Samples dissolved in DMSO diluted with acetonitrile or methanol were injected with a syringe pump at a flow rate of 240 μl/h.

The individuality of the obtained substances was confirmed by TLC on Silufol UV-254 plates in the benzene–ether–acetone (10:9:1) system or acetone–hexane (2:3) system; the chromatograms were stained using iodine vapour. The initial reagents were purified by distillation before use.

The optimisation of the geometric parameters of the equilibrium states of sodium oxoenolate and metal complexes was carried out using the following two methods: density functional theory (DFT) and self-consistent field (SCF). When calculating using the SCF method, the aug-cc-pVDZ basis was used, while the DFT method used the PBE/DZP approximation. Accounting for solvents was carried out according to the PCM model, in the case of compounds **1a**, **1b** – benzene and water, for compounds **2a–2f** – water. The relative formation energies of the structures **2a–2f** were calculated using the following equations

$$\Delta G°(E) = G°(E)(\mathrm{MeX}) - G°(E)(\mathrm{Me}^{2+}) + G°(E)(2\mathrm{X}^{-});$$

$$\Delta G°(E) = G°(E)\Sigma_{\mathrm{pr}} - G°(E)\Sigma_{\mathrm{reag}}\ [17].$$

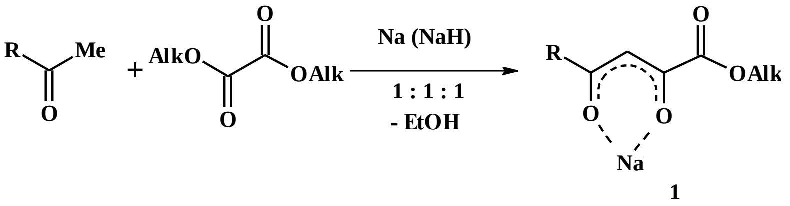
The calculations were performed in the FireFly 8.1 software package.

RESULTS AND DISCUSSION

The condensation of alkyl(aryl)methyl-ketones(3-methylbutanone-2 and acetophenone) with dialkyl oxalates (diethyl oxalate and di-*n*-butyloxalate) in the presence of sodium or sodium hydride in benzene or toluene at a ratio of the starting reagents 1:1:1 yielded sodium 1-alkoxy-1,4-dioxo-2-alkenolates (**1**) (Fig. 1).

New bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane - 2,4-dionato)-metals (II) (**2**) were synthesised by complex formation of sodium oxoenolates (**1**) with salts of zinc (II), copper (II) and nickel (II) in an aqueous medium with the initial ratio of reagents of 2:1 (Fig. 2).

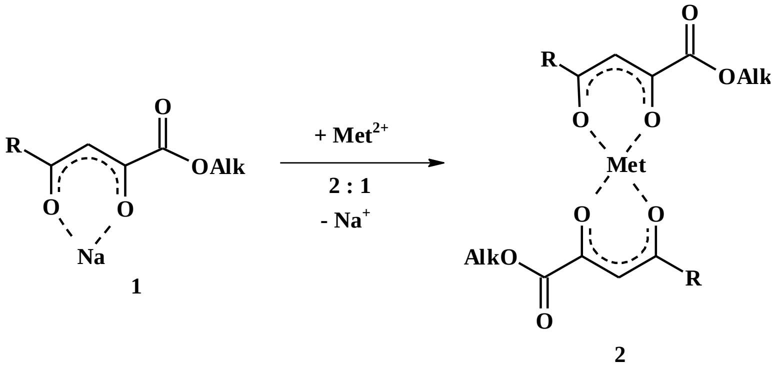
The structure of the obtained sodium oxoenolates (**1**) and metal (II) complexes (**2**) based on them was confirmed by means of IR, NMR^{1}H-, NMR^{13}H-spectroscopy, as well as mass spectrometry[1,2].



R = i-Pr (1a), Ph (1b); Alk = n-Bu (1a), Et (1b)

Fig. 1. Scheme of the synthesis of 1-alkoxy-1,4-dioxo-2-sodium alkenolates (1)

Рис. 1. Схема синтеза 1-алкокси-1,4-диоксо-2-алкенолятов натрия (1)



R = i-Pr (2a, 2b, 2c), Ph (2d, 2e, 2f); Alk = n-Bu (2a, 2b, 2c), Et (2d, 2e, 2f)
Met = Zn (II) (2a, d), Cu (II) (2b, e), Ni (II) (2c, f)

Fig. 2. Scheme of synthesis of bis-[4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato] metals (II) (2)

Рис. 2. Схема синтеза бис-(4-алкил(арил)-1-оксо-1-алкоксиалкан-2,4-дионато)металлов(II) (2)

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IR spectra of solid samples of sodium 1-alkoxy-1,4-dioxo-2-alkenolates (**1**) and bis-(4-alkyl(aryl)-1-oxo-1-alkoxyalkane-2,4-dionato) metals (II) (**2**) are characterised by the presence of a bright stretching band of the ester carbonyl group in the region of 1698–1687 cm^{-1} (for compounds **1a** and **1b**) and 172—1722 cm^{-1} (for compounds **2a–2f**). The bands in the region of 1597–1456 cm^{-1} are due to vibrations of monosubstituted aromatic rings (for compounds **1b** and **2d–2f)**. The high-frequency ether band arising due to vibrations of the C-O-C fragment appears in the region of 1267–1231 cm^{-1} (for compounds **1a** and **1b**) and 1317–1267 cm^{-1} (for compounds **2a–2f**).

In the NMR spectra of ^{1}H sodium oxoenolates (**1a** and **1b)** and zinc complexes (**2a** and **2d**) recorded in DMSO-d$_6$, the characteristic ethoxy fragments signals are observed for **1b** and **2d**) and n-butoxy fragments signals (for compounds **1a** and **2a**). Methine protons are identified by singlet signals in the region of 5.65–6.42 ppm. Proton signals of the monosubstituted aromatic rings for compounds **1b** and **2d** with phenyl fragments were recorded in the range 7.24–7.82 ppm.

The NMR spectra of ^{13}C sodium oxoenolates (**1a** and **1b)** recorded in DMSO-d$_6$, contain signals of alkyl carbon atoms in the range 13.5-30.1 ppm. The signals of aromatic carbon atoms (for compound **1b**) were recorded in the region of 126.4–142.2 ppm. Carbon atoms of carbonyl groups of ester fragments were detected at 168.7 (for n -butoxycarbonyl group of compound **1a**) and 170.6 (for ethoxycarbonyl group of compound **1b**).

In the mass spectra of synthesised compounds recorded in the electrospray mode, signals of protonated and cationised molecules are observed $[M+H]^+$, $[M+NH_4]^+$, $[M+Na]^+$ $[M+K]^+$.

In order to study the stability of the synthesised compounds, quantum-chemical calculations of their formation energies were carried out (Table 1). The calculations demon-strate the best convergence under the HF / aug-cc-pVDZ approximation. The solvation effects were considered only in the PBE / DZP approximation; in view of the complexity of the calculation, the solvation correction for the aug-cc-pVDZ basis was not considered in the SCF method. According to the obtained data, copper complexes have the greatest stability in the gas phase out of all the complexes tested. In general, according to the relative values of the formation energies, all compounds are stable, and metal complexes (**2**) are characterised by greater stability compared to sodium oxoenolates (**1**).

The values of the theoretically calculated dissociation constants of the obtained compounds are provided in Table 2. The obtained values indicate that zinc complexes (**2a, 2d**) possess the highest electrolytic dissociation capacity of all obtained metal complexes, while the compounds **1a, 1b** are relatively similar in terms of electrolyte strength.

Table 1

Absolute (E^0, G^0) and relative (ΔE, ΔG) formation energies of compounds 1a, 1b, 2a–2f

Таблица 1

Абсолютные (E^0, G^0) и относительные (ΔE, ΔG) энергии образования соединений 1a, 1b, 2a–2f

Compound	HF / aug-cc-pVDZ		PBE / DZP		PBE / DZP + PCM	
	E^0, Hartree	ΔE, kJ/mol	G^0 , Hartree	ΔE, kJ/mol	G^0, Hartree	ΔE, kJ/mol
1a	-887,923168	-143,3	-891,566532	-161,5	-891,584457	-137,6
1b	-922,301360	-145,2	-926,104389	-157,3	-926,125552	-139,0
2a	-3229,962850	-1315,8	-3237,721356	-1435,8	-3237,765320	-79,6
2b	-3091,107386	-1354,0	-3098,915975	-1556,8	-3098,947774	-922,5
2c	-2959,021762	-1270,8	-2966,768176	-1509,1	-2966,787241	-384,2
2d	-3298,717676	-1311,7	-3306,801958	-1448,6	-3306,847853	-80,5
2e	-3159,861688	-1348,6	-3167,994962	-1565,4	-3168,030201	-923,1
2f	-3027,776747	-1267,1	-3035,849309	-1523,3	-3035,872814	-393,1

Table 2

Dissociation constants of compounds 1a, 1b, 2a, 2c, 2d, 2f

Таблица 2

Константы диссоциации соединений 1a, 1b, 2a, 2c, 2d, 2f

Compound	PBE / DZP + PCM	
	Stage I	Stage II
1a	$9{,}5{\cdot}10^{-39}$	–
1b	$4{,}5{\cdot}10^{-38}$	–
2a	$1{,}7{\cdot}10^{-42}$	$1{,}4{\cdot}10^{-28}$
2c	$7{,}3{\cdot}10^{-96}$	$6{,}0{\cdot}10^{-82}$
2d	$8{,}0{\cdot}10^{-41}$	$7{,}9{\cdot}10^{-28}$
2f	$1{,}4{\cdot}10^{-95}$	$1{,}4{\cdot}10^{-82}$

CONCLUSIONS

During the study, potentially valuable sodium 1-alkoxy-1,4-dioxo-2-alkenolates and complexes of zinc (II), copper (II) and nickel (II) with carbonyl-containing ligands were successfully synthesised. Their structure was established using IR, NMR ^{1}H-, NMR ^{13}C-spectroscopy and high-resolution mass spectrometry methods. Quantum-chemical calculations of the formation energies and dissociation constants were carried out.

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Conflict interests

The authors declare no conflict of interests regarding the publication of this article.

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Contribution

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INFORMATION ABOUT THE AUTHORS

Elena A. Kunavina,
Cand. Sci. (Chemistry), Associate Professor,
Orenburg State University,
13, Pobedy Ave., Orenburg, 460018,
Russian Federation,
e-mail: kea20072007@yandex.ru

Sergey A. Peshkov,
Cand. Sci. (Chemistry), Associate Professor,
Orenburg State University,
13, Pobedy Ave., Orenburg, 460018,
Russian Federation,
e-mail: darvin156@mail.ru

Aybek Yu. Iskandarov,
Associate Professor,
Department of Chemistry and Methodology
of Teaching Chemistry,
Tashkent State Pedagogical University,
27, Bunyodkor Ave., Tashkent, 100183,
Uzbekistan,
e-mail: oybekiskandarov@mail.ru

СВЕДЕНИЯ ОБ АВТОРАХ

Кунавина Елена Александровна,
к.х.н., доцент,
Оренбургский государственный университет,
460018, г. Оренбург, пр-т Победы, 13,
Российская Федерация,
e-mail: kea20072007@yandex.ru

Пешков Сергей Алексеевич,
к.х.н., доцент,
Оренбургский государственный университет,
460018, г. Оренбург, пр-т Победы, 13,
Российская Федерация,
e-mail: darvin156@mail.ru

Искандаров Айбек Юлдашевич,
доцент, заведующий кафедрой химии
и методики ее преподавания,
Ташкентский государственный
педагогический университет,
100183, г. Ташкент, пр-т Бунедкор, 27,
Узбекистан,
e-mail: oybekiskandarov@mail.ru